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(54) A NEW OPTICAL BRIGHTENER OF THE BIS-STYRYL-BENZENE SERIES FOR POLYAMIDES

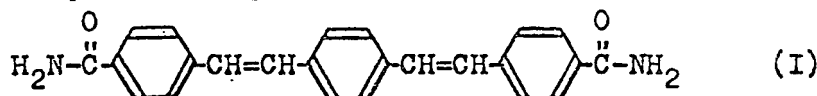
(71) We, BADISCHE ANILIN- & SODA-FABRIK AKTIENGESELLSCHAFT, a German Joint Stock Company of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a new optical brightener of the bis-styrylbenzene series which is suitable for the optical brightening of synthetic polyamides.

It is known that bis-styrylbenzenes whose terminal benzene nuclei bear free or esterified carboxyl radicals or a nitrile group can be used for stabilizing polyamides. Moulding materials are thus obtained which have an improved heat distortion temperature. It is a disadvantage however that such moulding materials have a troublesome green tinge.

It is also known that 1,4-bis-styrylbenzenes bearing alkyl, aryl, aralkyl and/or hydroxyl groups and/or halogen atoms can be used as optical brighteners for macromolecular organic substances. The brightening effect achieved therewith however leaves much to be desired.

The present invention provides the novel compound having the formula (I):—



which may be used for optically brightening synthetic polyamides in the melt.

The new compound may be prepared for example by reacting terephthalaldehyde with *p*-chloromethylbenzamide in the manner of the Wittig reaction. The *p,p'*-dicyano compound corresponding to the formula (I) may also be prepared by a Wittig reaction and partly hydrolysed to the *p,p'*-diamide.

The compound having the formula (I) is used for the optical brightening of polyamides by incorporation therein in amounts of from 0.001 to 0.2%, preferably from 0.005 to 0.1% by weight with reference to the weight of the final polyamide. The compound having the formula (I) may be added to the polyamide-forming starting materials before or during the polycondensation reaction. It is also possible however to add the compound having the formula (I) in fine division to the already prepared polyamides, particularly to dust or drum it onto the polyamide which is in the form for example of delustered or transparent granules, chips or powder, and then to melt the treated polyamide and process it by any process conventionally used for thermoplastics.

Mixtures of polyamides with the compound having the formula (I) may however be prepared which contain a much higher percentage of the optical brightener than that specified above (these being known as masterbatches). Moulding materials having the desired brightening effect can be prepared without difficulty by diluting the masterbatches with the appropriate amount of polyamide.

[Price 25p]

The polyamides to be given an optical brightening may be the known polyamides obtained by polycondensation of dicarboxylic acids and diamines or ω -aminocarboxylic acids and also by polymerisation of lactams. The conventional dicarboxylic acids for this purpose are aliphatic dicarboxylic acids having four to eighteen carbon atoms as for example adipic acid, suberic acid, sebacic acid, dodecane dicarboxylic acid and corresponding substitution products such as α,α -diethyladipic acid, α -ethylsuberic acid, heptadecane dicarboxylic acid-1,8 or heptadecane dicarboxylic acid-1,9 or mixtures of the same and also dicarboxylic acids containing cycloaliphatic or aromatic ring systems. Examples of suitable diamines are pentamethylenediamine, hexamethylenediamine, heptamethylenediamine, octamethylenediamine and C-substituted and/or N-substituted derivatives of these amines such as N-methylhexamethylenediamine, N-ethylhexamethylenediamine and 1,6-diamino-3-methylhexane, and cycloaliphatic or aromatic diamines such as *m*-phenylenediamine, *m*-xylylenediamine or 4,4'-diaminodiphenylmethane. In the monomers, the bridging groups between the two carboxylic acid groups or amino groups may be interrupted by heteroatoms.

Linear polyamides may however also be used which have been prepared by conventional methods by acid or hydrolytic polycondensation or if desired by activated anionic polymerisation of lactams having five to thirteen ring members. Examples of such lactams are pyrrolidone, caprolactam, oenanthalactam, capryllactam, laurilactam and equivalent C-substituted lactams such as C-methyl- ϵ -caprolactam, ϵ -ethyl- ϵ -caprolactam or ζ -ethyloenanthalactam.

Copolyamides which have been prepared by a conventional method from two or more lactams having five to thirteen ring members are also suitable. Such copolyamides include those prepared by cocondensation of a mixture of one or more lactams with at least one dicarboxylic acid diamine salt, for example caprolactam, hexamethylene diammonium adipate and 4,4'-diaminodicyclohexylmethane adipate. Other suitable copolyamides include polycondensation products of salts of the type diamine/dicarboxylic acid which have been prepared from at least three polyamide-forming starting materials.

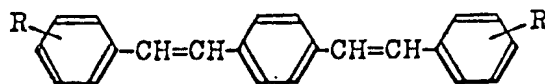
The compound having the formula (I) has outstanding resistance to high temperature, a high degree of whiteness and good light fastness. It imparts these useful properties to polyamides which have been optically brightened therewith. The superiority of the compound having the formula (I) as an optical brightener is shown by the following comparative test.

Nylon-6 granules have 0.075% by weight (with reference to the nylon-6) of each of the compounds set out in the following Table homogeneously incorporated under constant conditions and the granules are spun from an extruder.

The degree of whiteness and the shade of colour of the resultant fibres are judged visually and the brightening effect is assessed according to the following scale:

0 = no brightening
1 = slight brightening
2 = medium brightening
3 = strong brightening
4 = very strong brightening.

The compounds tested all have the general formula



The compounds added are as follows:

A in which R = $-\text{CONH}_2$ in *o*-position
B in which R = $-\text{CONH}_2$ in *m*-position
C in which R = $-\text{CONH}_2$ in *p*-position (i.e. the compound according to the invention)
D in which R = $-\text{CN}$ in *p*-position
E in which R = $-\text{COOCH}_3$ in *p*-position
F in which no compound is added.

TABLE

Compound added	Brightening effect	Shade of colour
A	0	none
B	1—2	neutral white
C	4	neutral brilliant white
D	3	strong green tinge
E	3	greenish white
F	0	none

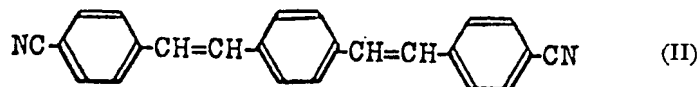
It is a particular advantage that the new optical brightener can be added to the starting materials for the polyamide because it does not interfere either with the hydrolytic polycondensation reaction or with the activated alkaline polymerisation of lactams. It condenses into the polyamide and is thus so firmly combined in the polymer that it cannot be removed in a subsequent extraction of the polymer for the removal of monomers and oligomers.

Polyamides which have been optically brightened by the use of the compound having the formula (I) exhibit a brilliant neutral, possibly slightly reddish white shade and good light fastness. Polyamides which have been optically brightened by the process according to the invention are suitable for the production of mouldings, film, sheeting, webs, ribbons, and fibres for a great variety of purposes.

The following Examples illustrate the invention. Statements as to parts and percentages in the following Examples relate to weight unless otherwise specified.

Example 1

(a) The production of 1,4-bis-(4'-cyanostyryl)-benzene (II): —

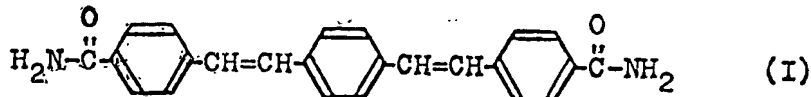


400 parts of 30% solution of sodium methylate in methanol is allowed to flow with vigorous stirring into a solution of 134 parts of terephthalaldehyde and 506 parts of diethyl *p*-cyanobenzylphosphonate in 800 parts of dimethylformamide. Yellow crystals separate after a short time. The contents of the vessel are stirred for one hour, then adjusted to a pH value of 7 with glacial acetic acid, diluted with 1000 parts of methanol and suction filtered. Upon recrystallisation from dimethylformamide, 272 parts (81.5% of the theory) of the compound having the formula (II) is obtained; it has a melting point of 278° to 279°C.

The phosphonic acid ester used as the starting compound may be prepared as follows:

152 parts of *p*-cyanobenzyl chloride is dissolved in the smallest possible amount of benzene. This solution is allowed to flow into 185 parts of triethyl phosphite which has been heated to 140°C. Benzene and the ethyl chloride formed are distilled off through a column; the residue is heated for one hour at 180°C. and then distilled at subatmospheric pressure. 218 parts of diethyl *p*-cyanobenzylphosphonate passes over as a viscous colourless oil at a pressure of 0.2 torr between 144° and 146°C. and soon solidifies to crystals having a melting point of 38° to 40°C.

(b) The production of 1,4-bis-(4'-carbamidostyryl)-benzene (I): —



A mixture of 332 parts of 1,4-bis-(4'-cyanostyryl)-benzene, 3300 parts of di-propylene glycol, 276 parts of anhydrous potassium carbonate and 36 parts of water is heated for five hours at 195° to 200°C. and then poured with vigorous stirring into a mixture of 10,000 parts of water and 450 parts of concentrated hydrochloric acid (38%). After having been stirred for two hours at 50° to 55°C., the whole is suction filtered and the precipitate is washed with 5000 parts of hot water. 360 parts (98% of the theory) of the compound having the formula (I) is obtained; it has a melting point of 380° to 385°C. and elementary analysis gives the following result:

$C_{24}H_{20}N_2O_2$ (molecular weight: 368)
 calculated: C 78.2 H 5.4 N 7.6 O 8.7
 found: 78.0 5.6 7.3 8.6.

Example 2

0.05 part of 1,4-bis-(4'-carbamidostyryl)-benzene is dusted onto 100 parts of polycaprolactam granules. The polymer prepared in this way is then melted at 270° to 280°C. in a screw extruder having a spinneret fitted thereon to form a homogeneously molten material which is spun into filaments and a melting temperature of about 245°C. The filaments are wound up and drawn in the ratio 1:3.8. They have the same physical properties as filaments which do not contain any 1,4-bis-(4'-carbamidostyryl)-benzene but exhibit a very good brightening effect with clearly improved brightness.

Example 3

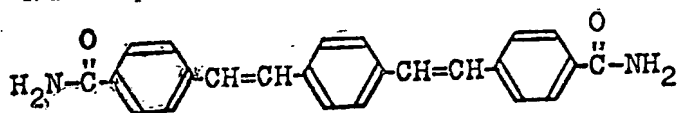
10,000 parts of a polyamide prepared from hexamethylenediamine and adipic acid and which is in the form of chips is mixed well with 30 parts of titanium dioxide and 3 parts of 1,4-bis-(4'-carbamidostyryl)-benzene in a mixing vessel. The chips treated in this way are placed in an appropriate vessel, atmospheric oxygen is removed therefrom and the chips are melted at 270°C., the melt is extruded through a spinneret and the cooled filaments are wound up on a bobbin. Filaments prepared in this way exhibit a very good brightening effect which is resistant to heat-setting and has good light fastness.

Example 4

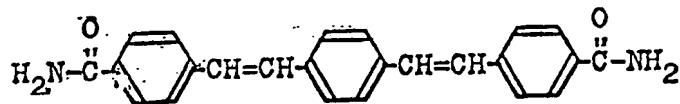
10,000 parts of epsilon-caprolactam, 300 parts of water, 40 parts of titanium dioxide and 2 parts of 1,4-bis-(4'-carbamidostyryl)-benzene are heated under nitrogen in a stirred autoclave for eight hours at 260° to 280°C. under autogenous pressure, then expanded to atmospheric pressure and further condensed for two hours at this temperature. The polyamide melt obtained is extruded through a sheeting die, quenched in water, granulated and dried. The moulding material which can be further processed under conventional conditions has a greatly increased degree of whiteness as compared with a polymer prepared under the same conditions but without the addition of 1,4-bis-(4'-carbamidostyryl)-benzene. The K value of the moulding material obtained is 70; a product not having the addition according to the invention has the same value of 70. There has therefore not been any deterioration in the quality of the material represented by the K value caused by introduction of the 1,4-bis-(4'-carbamidostyryl)-benzene.

WHAT WE CLAIM IS:—

1. The compound having the formula:



2. A process for the optical brightening of polyamides wherein the compound having the formula:



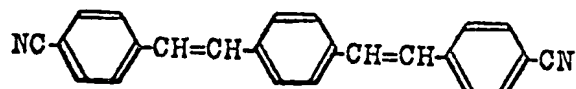
is added as an optical brightener to polyamide-forming starting materials before or during the polycondensation reaction or to the polyamide after the polycondensation in an amount sufficient to provide from 0.001 to 0.2% by weight of the compound in the final polyamide.

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3. A process as claimed in claim 2 carried out substantially as described in any of the foregoing Examples 2 to 4.

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4. A process for the production of the compound claimed in claim 1 wherein the compound having the formula:



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is partially hydrolysed.

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5. A process as claimed in claim 4 carried out substantially as described in the foregoing Example 1.

6. A polyamide which has been optically brightened by adding the compound claimed in claim 1.

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